DETERMINATION OF 18 TO 22 MOLE ETHOXYMERS IN NINE MOLE ETHYLENE OXIDE ADDUCT OF *p*-NONYLPHENOL

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Analytical specifications for various ethylene oxide adducts of alkylated phenols are required by the Food and Drug Administration for Food Additive Regulations under the U.S. Food, Drug and Cosmetic Act. It therefore became necessary to develop a method for the quantitative determination of ethoxymers in the 20 mole region in certain specified molar adducts of ethylene oxide to *p*-nonylphenol.

Studies of the ethoxylation of nonylphenol have shown that ethylene oxide adds in such a way as to give a mixture of compounds with varying chain lengths. The molecular weights of these products are usually distributed according to Poisson's equation[1]. Other studies on the ethoxylation of glycol[2] and octylphenol[3] have shown a similar distribution, while that of fatty alcohols was found to be much broader.

Ethylene oxide adducts of *p*-nonylphenol up to and including the eight-mole ethoxymer can readily be separated and determined by gas–liquid chromatography[4]. Higher ethoxymers undergo decomposition and therefore are not amenable to this method of analysis. BÜRGER[5] has separated a number of ethylene oxide adducts of alkylated phenols and fatty amines, alcohols, and acids by thin-layer chromatography. KELLY AND GREENWALD[3] have separated the lower adducts of octylphenol on silicic acid chromatography columns. Molecular distillation[1] has been used successfully for the separation of adducts up to the molecular weight region of 500 to 600. With this background, the solution to the problem appeared to be in the direction of column and/or thin-layer chromatography.

The initial approach was to remove the lower ethoxymers (below 18 mole) on a silicic acid chromatography column. Higher ethoxymers would then be removed with a more polar solvent system. However, diagnostic thin-layer chromatography examination of the 18-plus mole ethoxymers revealed that a significant amount of lower ethoxymers was still present. Evidently a certain amount of tailing occurred on the column. Gradient elution with acetone–chloroform mixtures failed to overcome this problem.

With the unsatisfactory application of column chromatography, the use of thin-layer chromatography was attempted. In order to overcome the sample size limitations of thin-layer chromatography, a quantitative preparative method was used. By substituting alumina as the adsorbent instead of silica gel G, but retaining the solvent system of BÜRGER[5], resolution of the higher ethoxymers was possible.

EXPERIMENTAL

Preparative thin-layer chromatography plates, 20 × 20 cm were coated in the usual manner with Woelm alumina (acid grade) to a thickness of 1.0 mm. These were allowed to air-dry overnight. A predevelopment with methanol moved any U.V. absorbing impurities to the top of the plate. After activation of the plate for 1 h at 105°, it was ready for use.

One ml of chloroform solution containing 100 mg of Dowfax*9N9 nonionic surfactant (nine mole ethylene oxide adduct of *p*-nonylphenol) was applied to the plate from a pipet in a continuous band along a lightly scored line 3 cm above the base of the plate. Development was carried out with water saturated butanone-2. When the solvent front had advanced 14 cm, the plate was removed from the tank and air-dried overnight. The butanone-2 must be completely removed since concentration determination depends on an U.V. spectrophotometric procedure. Drying at 105° immediately after development was attempted; however, recovery of the added ethoxymers was approximately 60 %. Apparently there was some decomposition at this temperature in the presence of alumina. Recovery of Dowfax 9N20 applied to the alumina plate and recovered by the recommended procedure gave quantitative results within experimental error.

With the aid of a sharp spatula four bands were outlined and scraped from the plate. These were positioned 0.5 cm below to 1.0 cm above the origin, 1.0 cm to 2.0 cm, 2.0 cm to 3.0 cm, and 3.0 to 4.0 cm. Methanol was added to the respective fractions and the alumina was removed by filtration through a medium porosity sintered glass filter. Filtrates were diluted to 100 ml in a volumetric flask. Solutions were scanned on a Cary recording spectrophotometer, Model 14, from 260 mμ to 320 mμ in a 10 cm optical cell using methanol as the reference liquid. Using the base line technique and a 20 mole adduct of *p*-nonylphenol (Dowfax 9N20) as a standard, the concentration of the 18- to 22-mole ethoxymers (1.0 to 2.0 cm band on plate) was calculated.

RESULTS AND DISCUSSION

As shown in Table I, the concentration of the 18 to 22 mole ethoxymers in nine mole ethylene oxide adduct of *p*-nonylphenol is about 1 %. In order to be certain

TABLE I

CONCENTRATION OF 18 TO 22 MOLE ETHOXYMERS IN NINE MOLE ADDUCT OF *p*-NONYLPHENOL

Sample	*Percent*
A	1.6
A	1.5
B	0.9
B	1.4
C	1.3
D	1.1

that the correct ethoxymer fraction had been isolated, the solutions measured by ultraviolet spectrophotometry were evaporated to dryness and examined by diag-

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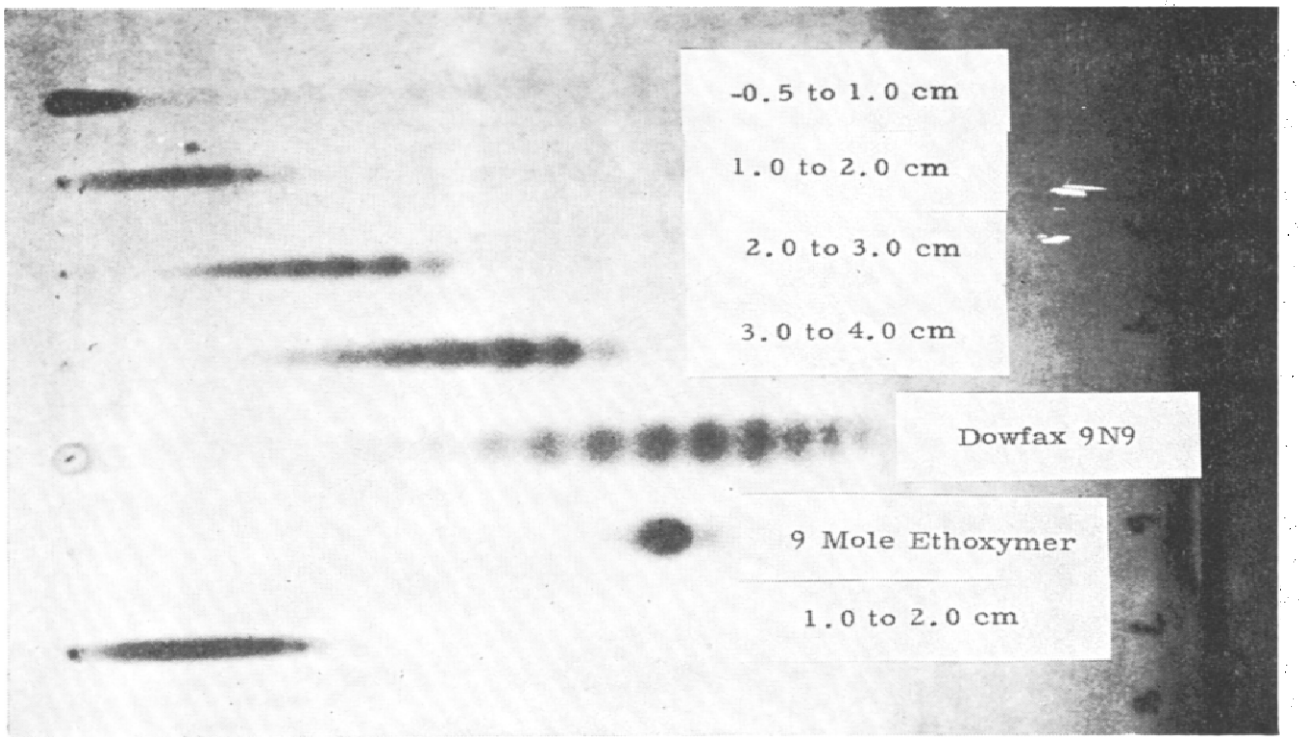

Fig. 1. Thin-layer chromatogram on 0.25 mm Woelm alumina (basic grade) with water saturated butanone-2 development. Shown are the various bands that were scraped from the plate. The chromatogram on the far right is the 1.0 to 2.0 cm band spotted at a higher concentration.

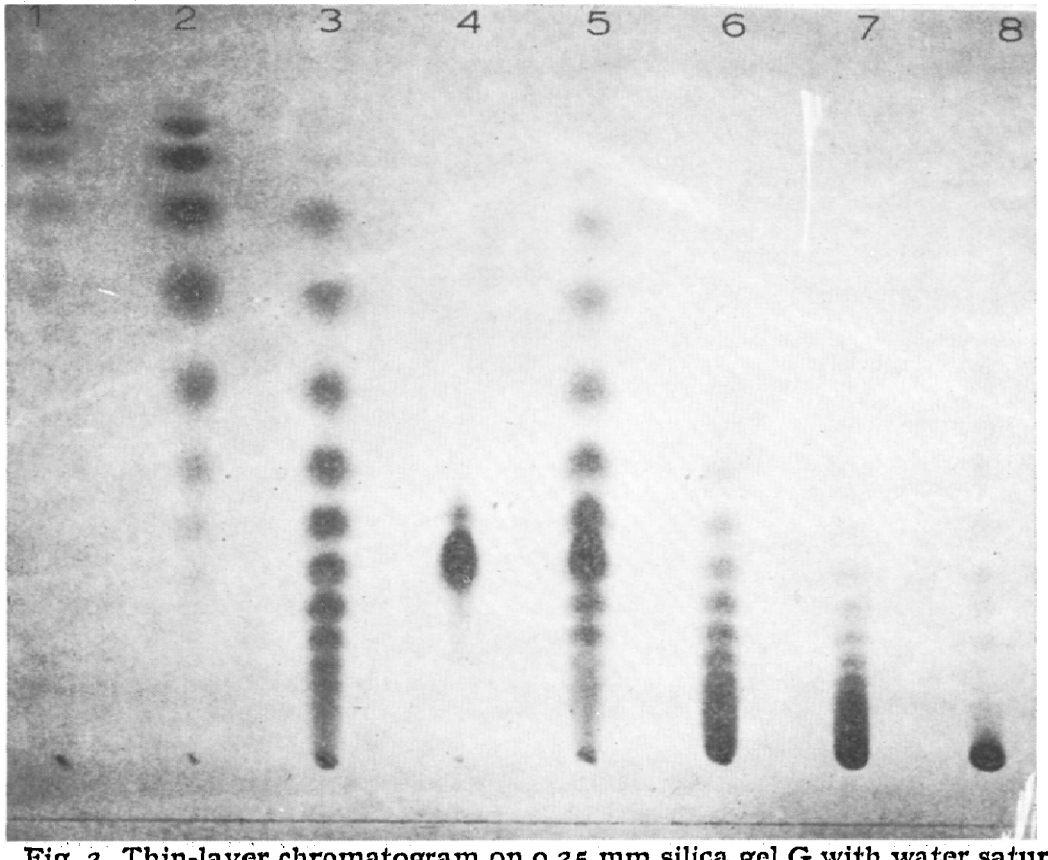

Fig. 2. Thin-layer chromatogram on 0.25 mm silica gel G with water saturated butanone-2 development. Samples represent 5 μl of 1% methanol solution. (1) Dowfax 9N2; (2) Dowfax 9N4; (3) Dowfax 9N9; (4) 9 mole ethoxymer; (5) Dowfax 9N9 plus added 9 mole ethoxymer; (6) Dowfax 9N15; (7) Dowfax 9N20; (8) Dowfax 9N30.

nostic thin-layer chromatography on 0.25 mm Woelm, basic grade, alumina, with water-saturated butanone-2 development. The ethoxymers were made visible by spraying with modified Dragendorff's reagent[5]. The results are illustrated in Fig. 1.

Before ethoxymer numbers could be assigned, some point of reference was necessary. This was accomplished by isolation and identification of an ethoxymer of known composition. A gradient elution of Dowfax 9N9 on a silicic acid column was made with acetone in chloroform. No attempt was made to obtain a particular ethoxymer, but rather one having reasonable purity. Characterization of the ethoxymer was made by a combination of diagnostic thin-layer and gas–liquid chromatography, that is, from ethoxymer distribution by gas chromatography, ethoxymer numbers could be assigned to the thin-layer chromatograms of Dowfax 9N2 and 9N4. Therefore by examination of these adducts together with Dowfax 9N9 and the isolated ethoxymer, the ethoxymer number assignment could be made (see Fig. 2). It was judged a nine mole ethoxymer, that is, nine ethylene oxide units attached to the *p*-nonylphenol. By using this as a reference point, it can be seen in Fig. 1 that the band from 1.0 to 2.0 cm contains the 18 to 22 mole ethoxymers.

The use of Dowfax 9N20 as an ultraviolet spectrophotometric standard was considered valid, within the experimental error of the method. If the molecular distribution curve is near-symmetrical, the ultraviolet sensitivity should approximate that of a pure 20 mole ethoxymer of *p*-nonylphenol.

Experimental error for the analysis is estimated at 25 to 50 %. This is considered reasonable taking into account the system being investigated.

SUMMARY

The 18 to 22 mole ethoxymers of *p*-nonylphenol were separated from a nine mole adduct by preparative thin-layer chromatography on alumina. Concentration determination was made by ultraviolet spectrophotometry and found to be in the 1.0 to 1.5 % range. This is moderately higher than that calculated by Poisson distribution.

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